4   SOIL COLLOIDS

Soil mineral colloids, which include crystalline and noncrystalline silicate minerals and hydrated oxides of aluminum and iron (also manganese in some soils), are responsible for many of the physical, physicochemical, and chemical properties exhibited by the soils. Soil colloids are particularly important in determining the capability of a soil to absorb and hold plant nutrients (both cations and anions), thereby restricting their rate of loss by leaching. An understanding of the structure and properties of colloids is therefore important in soil fertility management.

4.1. CLAY MINERALS

As the name indicates clay minerals are found in the clay fraction of the soil. All clay minerals are made up of layers of Si-tetrahedra and Al-octahedra (Figure 4.1) and are therefore known as layer silicates. Broadly, there are two major kinds, namely, minerals having one layer each of Si-tetrahedra and Al-octahedra (1:1 layer silicates) and those having one layer of Al-octahedra and two layers of Si-tetrahedra (2:1 layer silicates).

As shown in Figure 4.1, the dimensions of the void created by packing of four O^{2-} ions in tetrahedral configuration can accommodate one Si^{4+} ion. However, in the formation of a clay mineral or in its weathering, sometimes an Al^{3+} ion may substitute for an Si^{4+} ion. Since the charge on the Si-tetrahedral layer is neutral with Si^{4+}, substitution by Al^{3+} lowers the positive charge by one unit or it creates the negative charge of one unit. Such ionic substitution with cations of similar size is known as isomorphous substitution. Since the charge created by isomorphous substitution is due to the change in structure of the clay mineral, this is known as permanent change. Ionic substitution of Al^{3+} in the octahedral layers by Mg^{2+} or Fe^{2+} may also occur creating different kinds of clay minerals that also exhibit different physical and chemical properties. The ideal 2:1 layer silicates have a total cation charge of 22 (100 + 2 OH for pyrophillite) (see Table 4.2); +6 with octahedral sheet and +16 with the tetrahedral sheets. The total cation charge of +6 in the octahedral layer can be satisfied with two trivalent cations (Al^{3+}) or three
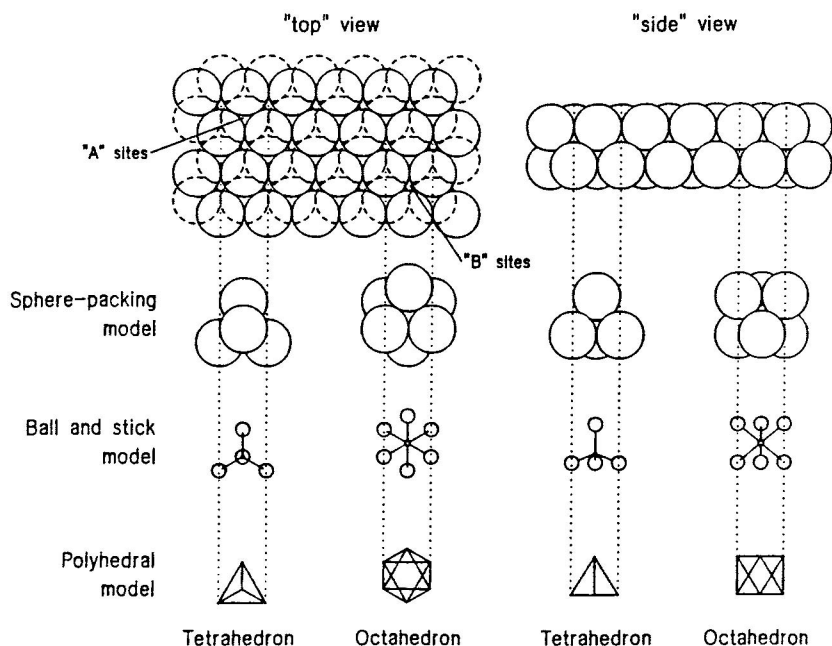
Figure 4.1. Octahedra and tetrahedra as a consequence of two planes of close-packaged spheres and three ways of representing octahedra and tetrahedra. (Adapted from Schulze, 1989.)

divalent cations (Mg^{2+}, Fe^{2+}). When a trivalent ion such as Al^{3+} is involved, only two out of three sites are filled in the octahedral layer and the arrangement or mineral is called dioctahedral. However, when a divalent ion such as Mg^{2+} or Fe^{2+} is involved, all three sites are filled and such an arrangement or mineral is known as trioctahedral.

Schematic diagrams of 1:1 and 2:1 layer silicates are given in Figure 4.2. In 1:1 layer silicates there are three planes of anions: (1) basal plane of O's, formed by the bases of a Si-tetrahedral sheet; (2) a central plane of OH's of Al-octahedral sheet and shared O's of tetrahedral sheet; and (3) a top plane of OH's of Al^{3+}-octahedral sheet. The tetrahedral and octahedral cations occupy their appropriate places. In 2:1 layer silicates there are four planes of anions (O, OH). Names and a brief description of important clay minerals follow.

4.1.1. The 1:1 Layer Silicates

4.1.1.1. Kaolinite

Kaolinite is the most common member of this subgroup. It is a dioctahedral 1:1 layer silicate and contains Al^{3+} in the octahedral and Si^{4+} in the
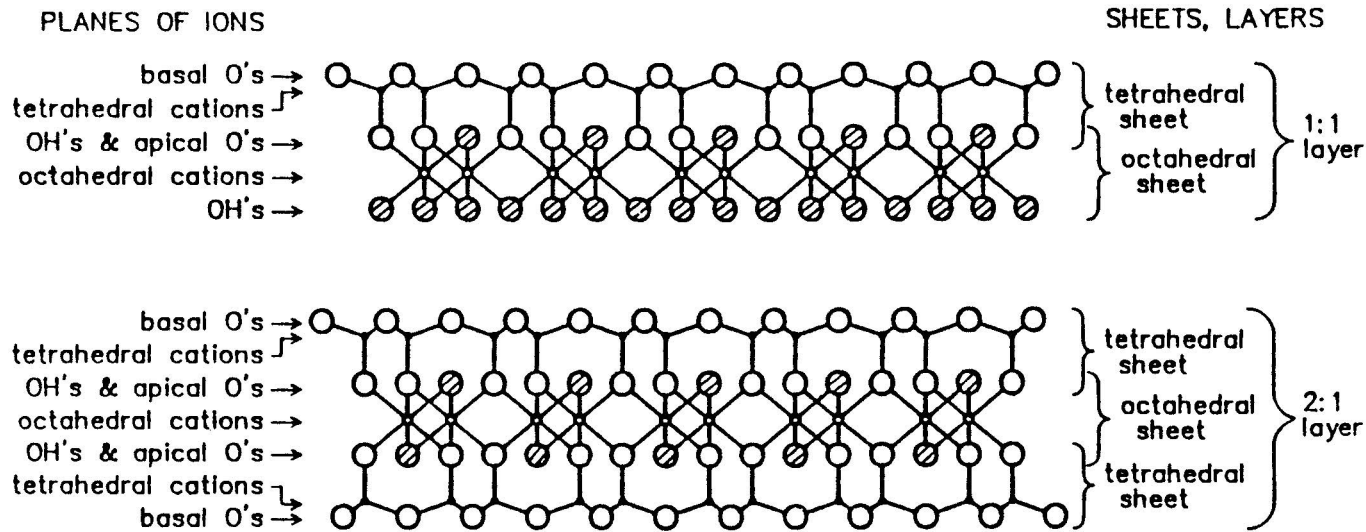
Figure 4.2. Phyllosilicate nomenclature. (Adapted from Schulze, 1989.)

Table 4.1 Particle Size, C-Axis Spacing and Surface Area of Some Clay Minerals

Minerals	Particle size (μm)	External surface ($m^2\ g^{-1}$)	Internal surface[a] ($m^2\ g^{-1}$)	C-axis spacing (nm)
Kaolinite	0.5–5.0	10–30	—	0.7
Smectite	0.01–1.0	70–120	550–650	1.0–2.0
Illite	0.2–2.0	70–100	—	1.0
Vermiculite	0.1–0.5	50–100	500–600	1.0–1.5
Chlorite	0.1–2.0	70–100	—	1.4

[a]This is a property of expanding-layer silicates.

tetrahedral sites (Figure 4.3). The Unit cell* formula is $Al_2^{3+}Si_2^{4+}O_5^{2-}(OH)_4^-$, which is charge neutral (14 positive and 14 negative charges). Consequently, the cation exchange capacity (CEC) is very low (2 to 5 cmol kg^{-1})** and generally due to OH^- on broken edges. Soils having kaolinites as the dominant mineral are generally less fertile. Thus a 1:1 layer is electrically neutral, and adjacent layers are held together by electrostatic binding between the basal O's of the tetrahedral sheet and the OH's of the adjacent octahedral sheet.

Kaolinite crystals are hexagonal in shape and range from 0.10 to 5 μm across; mostly in the 0.2 to 2 μm range (Table 4.1). The C-axis (interlayer) spacing is 0.7 μm or 7 angstroms.

Kaolinite is formed in soils by weathering of 2:1 layer silicates and other minerals such as feldspars. Soil parent materials such as clayey sediments may also contain kaolinite. Kaolinite is found in more weathered soils such as ultisols and oxisols and is thus abundant in tropical and subtropical regions of the world.

4.1.1.2. Halloysite

In halloysite the 1:1 layers are separated by a layer of H_2O molecules (Fig. 4.3). Halloysite often occurs as tubular or spheroidal particles. It is usually found in soils formed from volcanic deposits, soils in the Andept sub-order. Halloysite easily weathers to kaolinite.

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* A unit cell is the smallest particle of a mineral containing all its physical and chemical properties. The 3-dimensional arrangement of the unit cells defines the crystal lattice of a mineral and determines its shape and size. In clay minerals the units repeat themselves in a horizontal plane forming the layers and thus the name layer silicates.

** The earlier unit for expressing CEC was meq 100 g^{-1}. Since one cmol equals 10 milliequivalents, the numerical value remains the same. Thus 1 meq 100 g^{-1} is the same as 1 cmol kg^{-1}.
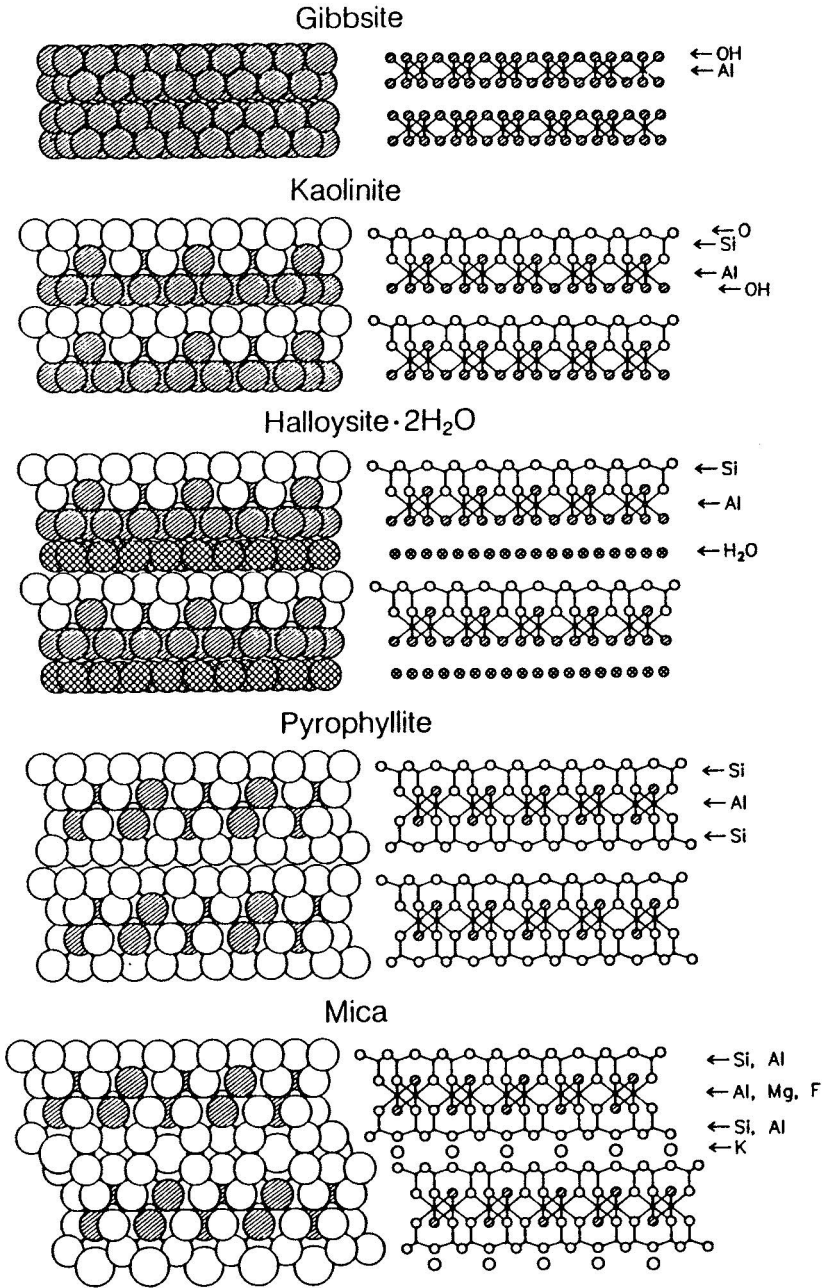
Gibbsite

← OH
← Al

Kaolinite

← Si ^{O}
← Al
← OH

Halloysite·2H₂O

← Si
← Al
← H₂O

Pyrophyllite

← Si
← Al
← Si

Mica

← Si, Al
← Al, Mg, F
← Si, Al
← K

Figure 4.3. Structural scheme of soil minerals based on octahedral and tetrahedral sheets. (Adapted from Schulze, 1989.)

Vermiculite and Smectite

← Si, Al
← Al, Mg, Fe
← Si, Al
← H_2O
← exch. Ca, Mg,
    Na, etc.

Chlorite

← Si, Al
← Al, Mg, Fe
← Si, Al
← Mg, Al, Fe

Hydroxy−interlayered
Vermiculite and Smectite
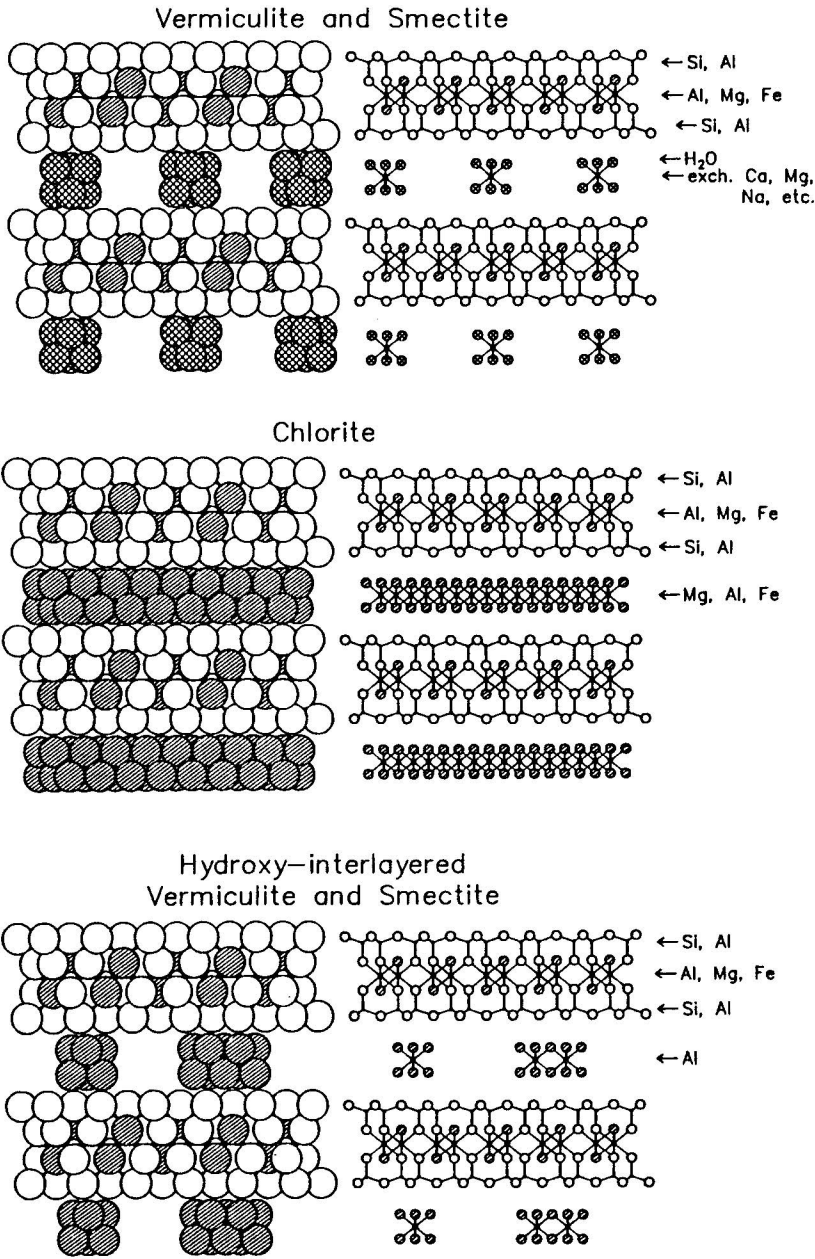
← Si, Al
← Al, Mg, Fe
← Si, Al
← Al

Figure 4.3. (continued).

4.1.2. The 2:1 Layer Silicates

As already explained, 2:1 layer silicates have one octahedral layer sandwiched between two tetrahedral layers. Different minerals in this group differ in the amount of isomorphous substitution and consequent negative charge. The most widespread group of minerals is smectites, which include montmorillonite, beidellite, nontronite, etc. Smectites are responsible for the high cation exchange capacity of Vertisols. Also these minerals have a great capacity to adsorb water and swell in the vertical (C-axis) direction and are therefore known as expanding clay minerals. The swelling on wetting and shrinking on drying property of Vertisols is due to smectites.

4.1.2.1. Pyrophyllite and Talc

Pyrophyllite is an ideal dioctahedral 2:1 layer silicate with Al in the octahedral sheet, while talc is trioctahedral with Mg in the octahedral sheet (Table 4.2). Since there is no isomorphous substitution, there is little negative charge on the mineral particles and these minerals are nonexpanding. Talc and pyrophyllite occur only rarely in soils.

4.1.2.2. Micas

Micas have structure similar to pyrophyllite or talc with the following distinct additional qualities:

1. There is considerable isomorphic substitution of Si^{4+} by Al^{3+}, Mg^{2+} or Fe^{2+} in the tetrahedral layer; nearly 20 to 25% sites have Al^{3+}, Mg^{2+}, and Fe^{2+}. This leads to a unit negative charge per unit formula (Table 4.2).
2. This excess negative charge is balanced by K^+ ions, which snugly fit in the hexagonal void created between two 2:1 layers. Since most of the negative charge is balanced by K^+, micas are nonexpanding in nature.
3. The micas have oxygen planes on both sides of their units. The six oxygens forming a hexagonal arrangement provide space just about the same size as oxygen (2.8 Å in diameter). Since the K^+ has a radius of 1.33 Å, it is the ion that snugly fits in the space. The next best choice is NH_4^+ ion with a radius of 1.48 Å. Thus soils having mica-derived minerals have the capacity to fix (immobilize) K^+ or NH_4^+ ions between the layers. Fixation and release of K^+ and NH_4^+ ions is important from the viewpoint of the availability of these ions to growing crop plants.

When the ion substituting for Si^{4+} in the tetrahedra is Al^{3+}, the mica is known as muscovite, while the mica containing Mg^{2+} in tetrahedral layer is

Table 4.2 Ideal Formula and Unit Negative Charge of Common Clay Minerals

Mineral	Ideal formula	Charge per unit formula	Fixed interlayer component	Net negative charge ($cmol\ kg^{-1}$)
1:1 Layer silicates				
Kaolinite	$Al_2Si_2O_5(OH)_4$	0	None	2–5
Antigorite	$Mg_3Si_2O_5(OH)_4$	0	None	
2:1 Layer silicates				
Pyrophyllite	$Al_2Si_4O_{10}(OH)_2$	0	None	
Talc	$Mg_3Si_4O_{10}(OH)_2$	0	None	
Muscovite (Mica)	$Al_2(Si_3Al)^{-1}O_{10}(OH)_2$	−1.0	K^+ 1.0	
Illite	$Al_2(Si_{3.2}Al_{0.8})^{-0.8}O_{10}(OH)_2$	−0.8	K^+ 0.7	15–40
Vermiculite	$(Al_{1.7}Mg_{0.3})^{-0.3}(Si_{3.6}Al_{0.4})^{-0.4}O_{10}(OH)_2$	−0.7	XH_2O	100–180
or	$(Mg_{2.7}Fe^{3+}{}_{0.3})^{+0.3}(Si_3Al)^{-1.0}O_{10}(OH)_2$	−0.7	XH_2O	
Smectites				
Montmorillonite	$(Al_{1.7}Mg_{0.3})^{-0.3}(Si_{3.9}Al_{0.1})^{-0.1}O_{10}(OH)_2$	−0.4	None	80–120
Beidellite	$(Al_2)(Si_{3.6}Al_{0.4})^{-0.4}O_{10}(OH)_2$	−0.4	None	80–120
Nontronite	$(Fe^{3+}{}_2)(Si_{3.6}Al_{0.4})^{-0.4}O_{10}(OH)_2$	−0.4	None	80–120
2:1:1 Layer silicates				
Chlorite	$(Mg_{2.6}Fe^{3+}{}_{0.4})^{+0.4}(Si_{2.5}Al/Fe_{1.5})^{-1.5}O_{10}(OH)_2$[a]		$Mg_2Al(OH)_6^+$ 1	15–40

Table 4.2 Ideal Formula and Unit Negative Charge of Common Clay Minerals

Mineral	Ideal formula	Charge per unit formula	Fixed interlayer component	Net negative charge (cmol kg^{-1})

[a]Unit negative charge is neutralized by unit positive charge on interlayer component.

known as phlogopite. Biotite mica on the other hand has Fe^{2+} and some Mg^{2+} as the substituting ions.

Micas in the clay fraction of soils and sediments often have poorer crystallinity, lower K and higher H_2O content than other 2:1 clays. Micas with Al^{3+} as the substituting ion are referred to as illite. Glauconite is similar to illite, but contains more Fe^{3+} and less Al^{3+}. The illites are dioctahedral and nonexpandible, and a part of their octahedral charge is balanced in the tetrahedral layer by additional Si beyond the ideal Si:Al ratio of 3:1 for muscovite. A representative formula is $K_{0.75}$ $(Al_{1.75}$ $RS_{0.25}^{2+}$ $(Si_{3.5}$ $Al_{l0.5})$ O_{10} $(OH)_2$, and the interlayer charge varies from 0.6 to 0.8 where R could be Mg^{2+} or Fe^{2+} (Fanning et al., 1989).

Micas weather to other minerals, particularly to vermiculites and smectites, and K^+ released during weathering is an important source of K for plants. Therefore soils derived from rocks rich in micas such as those in the Indo-Gangetic plains of India and Pakistan are rich in plant-available K.

4.1.2.3. Vermiculite

It is a 2:1 layer expanding silicate mineral with less ionic substitution than in micas. Thus the negative charge per unit mineral is less than 1; it is near 0.7* (range 0.6 to 0.9) (Table 4.2). In dioctahedral vermiculite, which is most abundant, the negative charge is nearly equally distributed in the octahedral and tetrahedral sheets. In the trioctahedral vermiculites, the octahedral sheet has a negative charge of –1.0, while the tetrahedral sheet has a positive charge (due to Fe^{3+} substituting for Mg^{2+}) of +0.3. Vermiculite has thus a net negative charge of 0.7. This charge attracts and holds cations such as Ca^{2+} and Mg^{2+} in the interlayer (Figure 4.3). These cations can be changed for other cations in soil solution, and the phenomenon is known as cation exchange. Cation exchange capacity (CEC) is an important property of a clay mineral and is equivalent to the net negative charge. Thus vermiculite has a CEC** of 100 to 180 cmol kg^{-1}. This high CEC gives vermiculites a high affinity for weakly hydrated ions such as K^+, NH_4^+ and Ca^{2+}. Consequently, soils rich in vermiculite have high K-fixation capacity. Vermiculites occur widely in soils.

Because of hydrated cations occupying the interlayer spaces, vermiculites have considerable expansion capacity and a large internal surface (500 to

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* These figures are near average. In nature there is likely to be considerable variation. This applies to all the minerals discussed in this chapter.

600 m^2 g^{-1}). The C-axis spacing is 1.0 to 1.5 nm depending upon the degree of hydration.

4.1.2.4. Smectites

The smectites are also 2:1 layer expanding silicates with a net negative charge of about 0.4, less than that for vermiculite (range 0.25 to 0.6). The dioctahedral (Al containing) smectite montmorillonite is the most common member in soils. In this mineral the negative charge is mostly created by the substitution of Mg^{2+} for Al^{3+} in the octahedral sheet, though there may be some charge on the tetrahedral sheet. In beidellite, which is also dioctahedral, the negative charge is due to ionic substitution of Al^{3+} for Si^{4+} in the tetrahedral sheet. This is also true for nontronite, which has Fe^{3+} in place of Al^{3+} in the octahedral sheet.

Smectites, because of their enormous expanding nature, have a very large internal surface (550 to 650 m^2 g^{-1} or more) and CEC (80 to 120 cmol kg^{-1}). They are the major clay mineral in vertisols such as black cotton soils of India and the blacklands of Texas. The shrink-swell behavior (swelling when wet and shrinking when dry) of vertisols, due to smectites, is a major problem in the management of these soils.

4.1.2.5. Chlorite

Chlorite is a 2:1:1 layer silicate. The additional layer occupies the inter-layer space between 2:1 layers. This layer consists of Mg-Al hydroxides with the general formula Mg_2Al $(OH)_6^+$ and has a unit positive charge that nearly balances the negative charge on the 2:1 layer. The net negative charge on 2:1:1 layer is thus hardly 0.1, giving it a low CEC (15 to 40 cmol kg^{-1}), similar to that of kaolinite.

Chlorites are infrequent in soils, and when present, they make up a small fraction of clay minerals. Chlorites are primary minerals and weather to form vermiculites and smectites.

** Because cation exchange capacity (CEC) of the clay minerals is an important property, it is imperative to understand how it is computed. Let us take the example of pyrophyllite. Its ideal formula is $Al_2Si_4O_{10}$ $(OH)_2$ (Table 4.2), having a formula weight of 360. If an Si^{4+} is replaced by an Al^{3+}, the formula weight changes to 359 and there will be a unit negative charge, which is equal to 1 mol (or 100 centimoles abbreviated as cmol). For 1000 g pyrophyllite the charge will be

$$\frac{1000}{359} \times 100 = 278 \text{ cmol kg}^{-1}.$$ This is the basis on which one estimates the CEC of a clay mineral.

Thus montmorillonite, having a net negative charge of 0.4, is likely to have CEC of 111 cmol kg^{-1}. Since different samples of various clay minerals differ in their net negative charge, it is conventional to give a range rather than a single value to CEC of a clay mineral.

4.1.2.6. *Polygorskite and Sepiolite*

These minerals are found in soils of arid and semiarid environments and have a fibrous morphology created by adjacent tetrahedral bands in a tetrahedral sheet pointing in the opposite direction.

4.1.3. Interstratified Silicate Minerals

Silicate minerals in soils do not always occur as discrete particles of mica, vermiculite, smectite, or kaolinite, but generally one, two, or three silicate minerals occur in mixtures or mixed layers and are known as interstratified minerals. The interstratified minerals may be two-component or three-component systems, for example, chlorite-vermiculite, chlorite-smectite, kaolinite-smectite, etc. The sequence of layers can be either regular or random, the latter being more common in soils.

4.1.4. Noncrystalline Silicates

Noncrystalline silicates include allophanes and imgolite. They are hydrated aluminum silicates (Demumbrum and Chesters, 1964) and are amorphous in nature and occur as a major constituent of young soils formed from volcanic ash. They are commonly found in Japan, New Zealand, New Guinea, Western Victoria, and South Australia (Norrish and Pickering, 1983) and in the B in the horizons of podzols and pozolized soils (Farmer, 1982). Allophanes have a SiO_2/Al_2O_3 ratio between 1.3 and 2.0 (this ratio for kaolinite is 2.0) and consists of spherules of 35 to 40 Å in outer diameter (Norrish and Pickering, 1983). Imgolite, on the other hand, has a tubular structure. Allophanes in B horizons of podzols are proto-imgolite in nature and consist of fragments of the imgolite tube wall (Figure 4.4) (Farmer, 1987). The CEC is 20 to 60 cmol kg^{-1}.

Allophanes have a very large surface area, values for which vary greatly depending on how it is determined. Aomine and Otsuka (1968) obtained values ranging from about 50 m^{2}g^{-1} using N$_2$ to 900 m^{2}g^{-1} using ethylene glycol. Soils containing much allophane may have very high water content (>100%), but they do not swell on wetting or shrink on drying. Loss of water is irreversible.

4.2. OXIDE MINERALS

Much of the research on the ionic charge of soil particles was carried out in the past on crystalline silicate minerals, which dominate the temperate region soils where most information in soil science has developed. However, in the second half of the twentieth century considerable interest has arisen in soils of the humid tropics (Van Raij and Peech, 1972; Morais et al., 1976; Keng and Uehara, 1974; El Swaify and Sayegh, 1975; Gallez et al., 1976),

a

		Si
○	○	Si
●	•	Al
◯◯		O
●●		OH
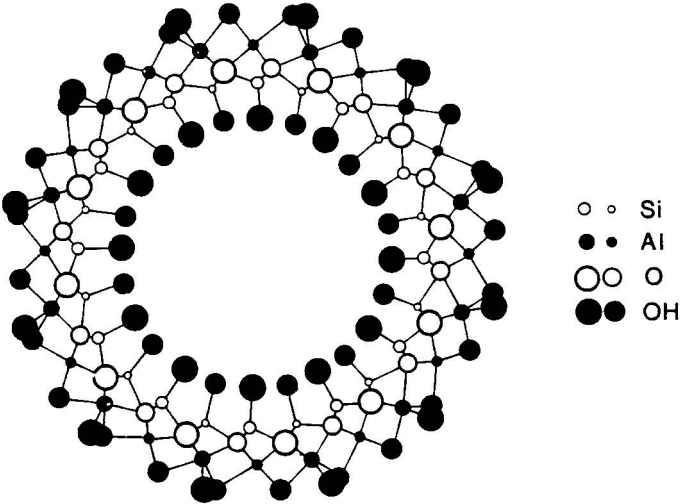
b
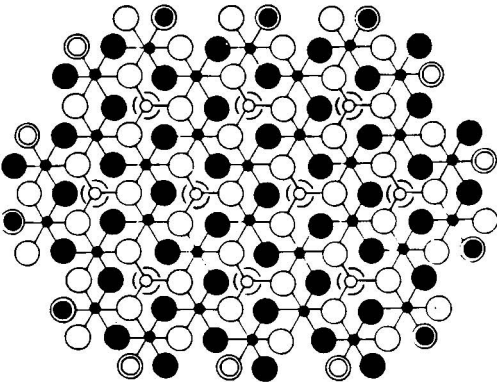
Successive atomic layers :

(1) ● OH   ◉ H₂O   **(2)** • Al

(3) ○ O,OH ◎ H₂O   **(4)** ○ Si

(5) ◌ OH

Figure 4.4. a. Cross section of an imogolite tube, showing atoms at two levels (large and small symbols). b. Proto-imogolite allophane is thought to consist of fragments of the imogolite wall, such as that shown here in plan. (From Farmer, 1987. Trans. 13th Int. Cong. Soil Sci. 5:63–68. With permission of the International Society of Soil Science, Vienna, Austria.)

which contain significant quantities of oxide minerals (oxides and hydroxides of Fe, Al, Mn, Ti, and Si). These soils come under the order ultisols and oxisols and occupy large tracts of level land in Latin America, Africa, and Southeast Asia. The high oxide content of these soils gives them the colors and names by which they have been known for time immemorial such as yellow soils, red soils, terra rosa, krasnozenes, etc. These soils have good physical conditions and are well drained, but have impoverished fertility due to excessive leaching of bases.

Oxide minerals differ from silicate minerals in the kind of ionic charge they possess. While silicate minerals carry "permanent charge" created by isomorphous substitution of metallic ions, most of the charge in oxide minerals is pH dependent and is therefore known as "variable charge." Variable charge is also present in small amounts in silicate minerals and humus. At some pH value an oxide mineral can have equal quantities of H^+ and OH^- ions, so that the net surface charge is zero in the absence of any specifically adsorbed ions; this pH is known as zero point of charge (ZPC) or isoelectric point. The ZPC for the common soil oxides is usually between pH 6.5 to 10.4 (Parks, 1965). Under acid conditions, an oxide is positively charged and can have an appreciable anion exchange capacity. This imparts to oxide minerals an ability to adsorb OH^- ions and therefore high buffering capacity. Consequently, soils having oxide minerals require large amounts of liming material. On the other hand, under alkaline conditions oxide minerals acquire a negative charge and exhibit cation exchange capacity as shown below:
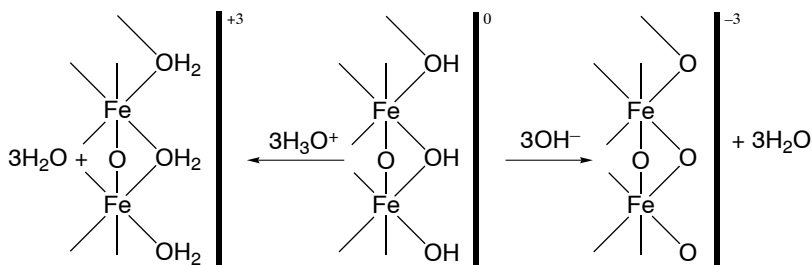
(From Parks and deBruyn, 1962)

The surface charge density for goethites and hematites at pH 4 in 1 M NaCl was between 1.8 and 4.9 $\mu eq\ m^{-2}$ (Atkinson et al., 1967; Atkinson, 1969). The specific surface area for goethites is 14 to 77 $m^2\ g^{-1}$, while that for hematite ranges between 34 and 45 $m^2\ g^{-1}$. Under warm climatic conditions with high rainfall organic matter decomposes rapidly, leaving oxide surfaces with a positive charge and incapable of retaining nutrient cations against leaching losses; such soils thus have impoverished soil fertility. Under such conditions application of silicate amendments might be useful, since silicate ions can be specifically adsorbed onto oxides, with a resultant increase in negative charge (Taylor et al., 1983).

The most common oxide minerals in soils are of Fe, Mn, Al, and Si. In some soils (not under cultivation) the oxides of Ti may also be present.

4.2.1. Iron Oxides

Iron oxides may be evenly distributed throughout the profile or may be concentrated in a particular horizon. They can exist as coatings on sand grains and crack faces, as constituents in cemented aggregates, or as discrete fine particles.

Iron is fairly mobile in the soil profile because of its soluble reduced Fe^{2+} form. Also it forms complexes with several anions. Iron therefore plays a vital role in the structure and fabric of a soil by cementing aggregates or by formation of concretionary layers, or iron-stone cappings. The most common soil iron oxides are goethite, lepidocrocite, hematite, maghemite, ferrihydrite, and magnetite. Magnetite (Fe_3O_4) exists as a residual primary mineral, while the other five minerals are products of pedogenesis.

Goethite (α - Fe OOH) is the most common mineral and is present in most soil types under diverse climatic conditions. It is the "yellow ochre" pigment responsible for a yellow-brown color in many soils, for example, yellow earths; it produces the yellow mottles in laterites (Davey et al., 1975).

Lepidocrocite (γ - Fe OOH) is less common than goethite. It is a common mineral in hydromorphic soils of the humid temperate regions, where it is often associated with goethite (Schwertmann and Fitzpatrick, 1977).

Hematite (α - Fe_2O_3) is a common mineral in the soils of arid and tropical regions, where the decomposition of organic matter is so rapid that it does not promote goethite formation. It is the "red ochre" responsible for red coloration of many soils such as terra rosas and red earths. It occurs often in association with goethite. In x-ray diffraction the presence of goethite or hematite can be recognized by a common line at 2.69 to 2.70 Å (Taylor et al., 1983).

Maghemite (γ - Fe_2O_3) is common in highly weathered soils of the tropics and subtropics, especially in soils formed on basic igneous rocks. This mineral generally contains a small percentage of ferrous iron but less than its isomorph magnetite, which generally contains close to the theoretical one-third of its total iron in the ferrous form (Fasiska, 1967).

Ferrihydrite (HFe_5O_8, $4H_2O$) is often found in drainage ditches and is often considered as having been formed by microbial decomposition of soluble Fe-organic compounds and subsequent hydrolysis and precipitation (Taylor et al., 1983).

The iron in soils originates from the weathering of iron-bearing silicates in which iron is generally present in the divalent state. Once separated from the silicate mineral, ferrous iron is subsequently precipitated and oxidized or oxidized and precipitated; the sequence of processes is important. In general, where oxidation precedes hydrolysis, the α -iron oxides, goethite and hematite, form. However, when hydrolysis and precipitation occur before oxidation, the R-oxides, lepidocrocite and maghemite, often occur. Possible pathways of iron

oxide formation under near pedogenic conditions as proposed by Schwerrt-mann and Taylor (1977) are shown in Figure 4.5. These processes may occur *in situ* where iron is released from silicates or after transportation in subsurface waters to other parts of the profile or landscape.
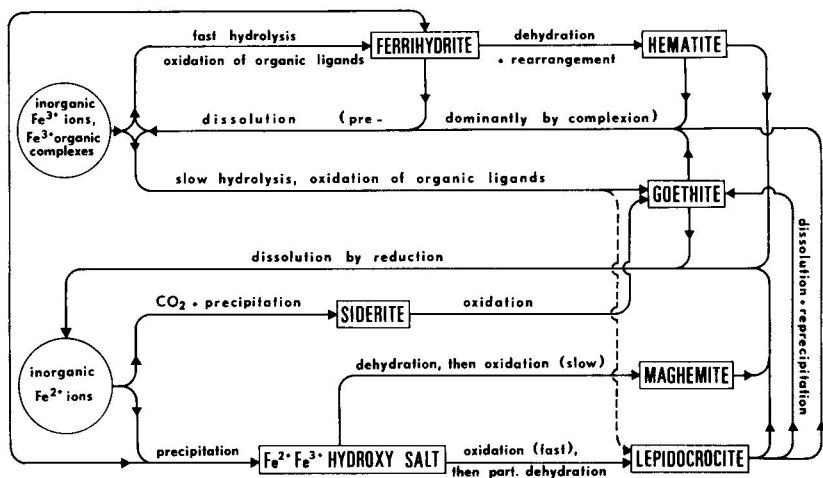

Figure 4.5. Possible pathways of iron oxide formation under near pedogenic conditions. (From Schwertmann and Taylor, 1977. *Minerals in Soil Environments*, J.B. Dixon and S.B. Weed, Eds., p. 160. With permission of Soil Science Society of America, Madison, WI.)

The strong affinity that iron oxides have for organic anions is of great importance from the viewpoint of soil fertility and crop production. Important points to be brought out are as follows:

1. The beneficial effect of organic manures, in part, may be due to the production of organic anions on decomposition, providing sites for phosphate ions to sorb on iron oxides. Regarding adsorption of phosphate on iron oxides, both mono (a) and bidentate (chelated) (b) complexes may exist, explaining different bonding strengths (b>a) and the partial irreversibility of phosphate sorption (Hingston et al., 1974).

2. Also, as explained earlier, since the charge on iron oxides is pH dependent, both anions and cations are retained. Furthermore, the adsorption also depends upon the concentration of different ions in soil solution. Results from a study by Bowden et al. (1973) are shown in Figure 4.6. Phosphate adsorption was greater in the acidic pH range and declined as pH increased; adsorption of silicate fol-

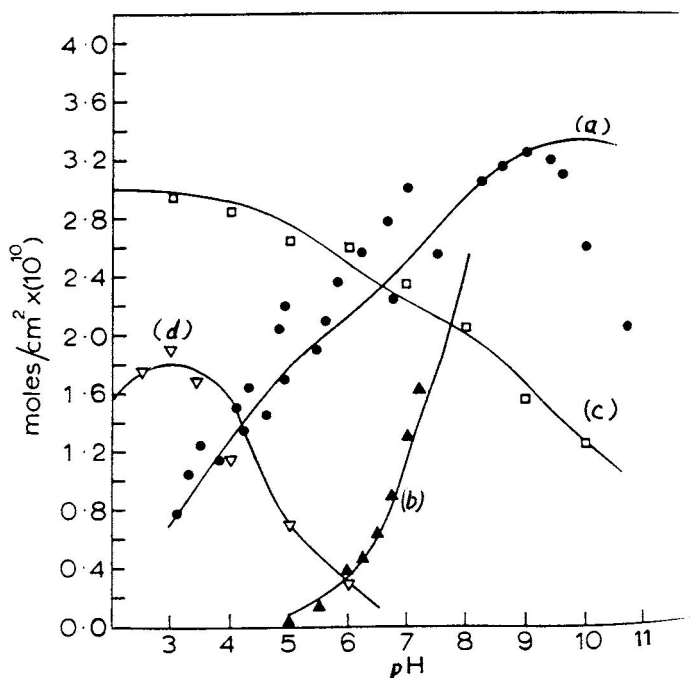lowed the reverse pattern, being greater at alkaline pH. Zn adsorption was greatest between pH 7 and 8.

Figure 4.6. Adsorption on goethite as a function of pH; (a) silicate, 8×10^{-4} _M_ (0.1 _M_ NaCl); (b) zinc, 1×10^{-4} _M_ (0.1 _M_ NaCl); (c) phosphate, 3.2×10^{-4} _M_ (0.01 _M_ NaCl); (d) 2,4-D, 3×10^{-4} _M_ (0.01 _M_ NaCl); —, present model. Points are from experimental data: d, silicate; m, zinc; h, phosphate; „ 2,4-D. (From Bowden et al. 1973. Nature (London) 245:81–82. With permission.)

3. Complex formation of iron oxides with organic anions makes iron more mobile.
4. Iron oxide-organic anion complexes improve soil structure as judged by the formation of aggregates (Table 4.3).
5. The cation exchange capacity of soil organic matter is reduced by iron oxide-organic anion complex formation, and therefore the ability of the surface soils to retain plant nutrients is reduced.
6. Figure 4.6 also shows the effects of pH on adsorption of 2,4-D, which was maximum at pH 3. Thus many herbicides and pesticides lose their efficiency by reaction with iron oxides, and they may persist undecomposed for long periods in such soils.

Table 4.3 The Influence of Synthetic Iron Oxide Addition to a Loess Soil (86% Silt) on the Formation of 1–2 mm Water-Stable Aggregates after Air Drying

Fe-oxide	Amount added (% Fe)	Oxalate solubility[a], (% of total Fe)	Aggregates (1–2 mm, %)
No addition	0.0	—	18
Ferrihydrite	11.0	100.0	48
Ferrihydrite	2.3	100.0	83
Lepidocrocite	1.0	68.0	53
Goethite	1.0	0.1	17
Goethite	0.6	93.0	77
Hematite	1.0	0.1	20

[a]Taken as a measure of degree of crystallinity.

From Schahabi and Schwertmann, 1970. Z. Pflanzen. Dueng Bodenk. 125:193–204.

4.2.2. Manganese Oxides

Manganese occurs in a number of oxidation states, but only the cationic oxidation states (positive) 2, 3, and 4 occur in nature. A large number of oxides and hydroxides occur in nature, where there is an extensive substitution of Mn (II) and Mn (III) for Mn (IV) and of OH^- for O^{2-}. The structures of manganese oxides can change with a change in the oxidation state of Mn. This and their intimate occurrence with iron oxides in soils make the determination of chemical composition of manganese oxides difficult.

As is the case with the iron oxides, manganese oxides also occur in soils as deposits in cracks and veins and as coatings and stains or as a cementing material in soil aggregates. Manganese oxides may also occur roughly as spherical nodules up to about 2 cm in diameter. These nodules contain considerable amounts of iron oxides, as well as some other minerals, and many have a concentric, layered structure suggestive of seasonal growth. Burns and Burns (1975) suggested that nucleation and growth of many manganese nodules is initiated by a deposit of ferrihydrite on a nucleating agent, followed by epitaxial growth of δ MnO_2 and ferrihydrite on each other.

Although a large number of Mn oxide minerals are known (Table 4.4), only a few occur in soils. It seems likely for soils that either δ MnO_2 or birnessite are formed first and that these minerals may recrystallize subsequently, under suitable conditions, to lithiophortite or todorokite or the cryptomelane group (Taylor et al., 1983).

A large amount of Mn in soil solution, as under submerged rice paddies, can lead to Mn-toxicity problems; manganese toxicity can be a constraint to plant growth on acid oxisols (Fageria et al., 1990).

Table 4.4 Some Manganese Oxide Minerals

Mineral name	Other names	Composition
Pyrolusite	β-MnO$_2$, polianite	MnO$_2$
Ramsdellite	—	MnO$_2$
Nsutite	γ-MnO$_2$, ρ-MnO$_2$	Mn(O, OH)$_2$
Birnessite	δ–MnO$_2$, manganous manganite, 7 Å manganite	Variable
Todorokite	—	Variable
Cryptomelane	α-MnO$_2$	K$_2$Mn$_8$O$_{16}$
Hollandite	α-MnO$_2$	Ba$_2$Mn$_8$O$_{16}$
Coronadite	α-MnO$_2$	Pb$_2$Mn$_8$O$_{16}$
Psilomelane	romanechite	BaMn$_9$O$_{16}$(OH)$_4$
Lithiophorite	—	(Al, Li)MnO$_2$(OH)$_2$
Groutite	α-MnOOH	MnOOH
Manganite	γ-MnOOH	MnOOH
Hausmannite	—	Mn^{2+}Mn$_2^{3+}$ + O$_4$

From Taylor et al. 1983. *Soils — Australian Viewpoint,* Academic Press, San Diego, CA, pp. 309–334. With permission of Academic Press, Inc.

4.2.3. Aluminum Hydroxides and Oxyhydroxides

A number of crystalline aluminum oxides or rather hydroxides and oxy-hydroxides are found in nature. Hsu (1977) suggested the term hydroxides for polymorphs of Al(OH)$_3$ and oxyhydroxides for polymorphs of AlOOH, and these terms are used in this chapter.

Crystalline Al-hydroxides exist in three polymorphs, namely, gibbsite, bayerite, and norstrandite. Only gibbsite is common in soils and bauxite deposits, although the presence of bayerite (Benter et al., 1963) and norstrandite (Wall et al., 1962) has been reported. Gibbsite is a major mineral in andosols in Japan (Wada and Aomine, 1966) and ultisols and oxisols of the tropics and subtropics and temperate regions (Rich et al., 1959). Bauxite deposits, dominated by gibbsite and to a lesser degree by boehmite or diaspore, are products of extremely advanced weathering (Hsu, 1977). All three polymorphs of Al-hydroxides are composed of the same fundamental units, which is two planes of close-packed OH- octahedra with Al^{3+} sandwiched between them. The Al^{3+} ions occupy two-thirds of the octahedral positions. The three polymorphs differ in the stacking of fundamental units. Gibbsite crystallites are usually well developed in the x and y (horizontal) directions, but limited in the z (vertical) direction and therefore appear as hexagonal plates. While bayerite crystallites usually take the form of a pyramid, nordstandite crystallites are often long, rectangular prisms.

Crystalline Al-oxyhydroxides are present in two polymorphs, namely, diaspore and boehmite. Both the polymorphs have double chains of HO-Al-O; the structural difference is in the arrangement of these double chains.

Large amounts of noncrystalline hydroxides and oxyhydroxides are also present in nature. These materials do not have a definite composition or structure, but exhibit properties similar to those of the crystalline Al-hydroxides and oxyhydroxides.

Anion adsorption and fixation properties of Al-hydroxides and oxyhydroxides are similar to those of iron oxides. The affinity of both iron oxides and Al hydroxides and oxyhydroxides for phosphate is well established (Wild, 1950). In addition to phosphate, sulfate is also adsorbed by gibbsite (Chao et al., 1964), but can be replaced by phosphate, which is held more tightly.

The role of Al-hydroxides and oxyhydroxides as cementing agents for soil aggregates is well documented (Saini et al., 1966; El Swaify and Emerson, 1975). Al-hydroxides decrease their positive charge, as well as their cementing effectiveness, with increasing pH. Iron oxides have a stronger tendency to crystallize than Al-hydroxides; the former is thus likely to be less effective than the latter in cementing effectiveness. For example, Saini et al. (1966) found that in Canadian soils (B horizons of podzols) the partial regression coefficient relating Al-oxides with aggregation was 1.84 times larger than that for iron oxides.

4.2.4. Silicon Oxides

Silica is the most abundant oxide in the lithosphere. The most common forms of silica found in soils are quartz, cristobalite, tridymite and the poorly crystalline opals. Thermodynamically, quartz is the only stable variety.

Because of its large particle size, and its relatively unreactive surfaces, quartz plays a negligible role in plant nutrition. It, however, has a definite role in determining soil texture and structure. Quartz can be identified by an X-ray diffraction peak at 3.34 Å.

4.2.5. Titanium Oxides

Three polymorphic forms of TiO_2 are found in soils, namely, rutile, anatase and brookite (Taylor et al., 1983). In addition, three combined oxides or titanites are: Ilmetite ($FeTiO_3$), Sphene ($CaTiSiO_5$) and Perovskite ($CaTiO_3$). Titanium is not an essential plant nutrient and these oxides have thus no effect on the nutritional status of a soil.

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